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(21) International Application Number: PCT/NL98/0003 (22) International Filing Date: 20 January 1998 (20.01.9) (30) Priority Data: 1005129 30 January 1997 (30.01.97) N  (71) Applicant (for all designated States except US): DSM N. [NLNL]; Het Overloon 1, NL-6411 TE Heerlen (NL).  (72) Inventors; and (75) Inventors/Applicants (for US only): MEIJ, Theodoor, He drik [NL/NL]; Broederschap 11, NL-8014 XB Zwolle (NL HOUWELING, Theodoor, Hendrik [NL/NL]; Broederschap 11, NL-8014 XB Zwolle (NL). DIAS, Aylvin, Jorge, A gelo, Athanasiu [GB/NL]; Sphinxlunet 11F, NL-6221 J. Maastricht (NL). JANSEN, Johan, Franz, Gradus, Ant nius [NL/NL]; Marisstraat 11, NL-6165 AP Geleen (NI VAN BENTHEM, Rudolfus, Antonius, Theodorus, Maris [NL/NL]; Sportlaan 9, NL-6141 BR Sittard (NL).  (74) Agent: SCHMEETZ, Marcel, Max, Hubertina, Johanna; Ctrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NI C54) Title: RADIATION-CURABLE COMPOSITION	CZ, EE, GE, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published  With international search report.  With amended claims.  DC-  OC-	PCT 6-30-99 EP 7-4-98
	nprising a mono or multi valent carboxylic ester of a $\beta$ -hydroxyalkylamide rived from an $\alpha$ , $\beta$ -ethylenically unsaturated carboxylic acid. A coating trisation and shows the desired chemical and mechanical properties.	

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### RADIATION-CURABLE COMPOSITION

5 The invention relates to a radiation-curable composition.

During radiation curing processes the transformation of the fluid applied film to a solid crosslinked network can be considered to progress through three distinct stages being induction, polymerisation and attainment of maximum cure plateau. (Chemistry and Technology of UV and EB formulations, Volume IV, Oldring, 1991, pages 8-12).

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Factors which improve or inhibit cure rate
are, for example, the lamp system (UV-dose, intensity,
wavelength, IR-content) and the chemical system
(reactivity, absorption, coating weight, pigmentation,
temperature, oxygen inhibition and substrate).

ror commercial coating operations, it is
necessary that the coating achieves a tackfree surface
within seconds or less, because the interval between
application of the coating and stacking or rewinding of
the coated substrate is very short. Failure of the
coating to achieve a non-tacky surface in this brief
interval will result in the layers of coated substrate
(in a stack or roll) sticking together ("blocking).

It is the object of the present invention to provide a coating composition having a high cure rate or rate of polymerisation and having the desired chemical and mechānical properies.

The radiation curable composition according to the invention comprises a mono or multi valent carboxylic ester of a  $\beta$ -hydroxyalkylamide group containing compound, in which the carboxylic ester is derived from an  $\alpha, \beta$ -ethylenically unsaturated carboxylic acid.

The composition according to the invention results in high maximum polymerization rates.

According to a preferred embodiment of the invention the compound is according to formula (I):

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where:

hydrogen, or a monovalent or polyvalent organic 15 A =group which is derived from a saturated or an unsaturated (C1-C60) alkyl group, or derived from an (C<sub>6</sub>-C<sub>10</sub>) aryl group,

hydrogen, an (C<sub>1</sub>-C<sub>8</sub>) alkyl group or Y =

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R1, R2, R3, R4 are, identical or different, hydrogen or a lineair, branched or cyclic (C1-C3) alkyl chain,

 $R^5$  = hydrogen,  $(C_1-C_5)$  alkyl;  $-CH_2OH$  or  $CH_2COOX$ ,

 $R^6, R^7 = \text{hydrogen}, (C_1 - C_8) \text{ alkyl}, (C_6 - C_{10}) \text{ aryl or COOX}$ 

= hydrogen or  $(C_1-C_8)$  alkyl and

= 1 or 2q

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R1, R2 or R3 may form part of a cycloalkyl group.

The organic groups in A may be substituted with, for example, ethers, esters, hydroxyl, amides, acids, amines or ketones.

Preferably, ester- or hydroxylgroups are applied as substitutents.

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Preferably, A is a monovalent organic group which is derived from a saturated  $(C_1-C_{12})$  alkyl group.

According to another preferred embodiment of the invention A is a polyvalent organic group derived from a saturated  $(C_2-C_{10})$  alkyl group or a  $C_6$ -aryl group.

Preferably, Y is hydrogen or methyl.

Preferably,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrogen or methyl.

 $R^5$  is preferably hydrogen or (m)ethyl.  $R^6$  and  $R^7$  are preferably hydrogen.

The compound applied in the invention generally has a number-average molecular weight (Mn) of between 140 and 2500, and preferably of between 450 and 1000.

The compound can be obtained, for instance, by an esterification reaction between a  $\beta$ -hydroxyalkylamide and an unsaturated carboxylic acid, at a temperature between, for example, 80°C and 140°C.

Preferably, 1 - 1.5 mol of acid are used per mole of hydroxide.

Preferably, the reaction takes place in the presence of an organic solvent, such as, for example, xylene, toluene or tetrahydrofuran.

preferably, the reaction takes place in the

presence of a stabilizing compound which prevents
polymerization of the unsaturated ester groups under
the conditions used for effecting this reaction. The
stabilising compound or a mixture of stabilising
compounds is generally used in amounts between about 50

and about 2000 ppm and preferably between 75 and 1000
ppm. They can be used in aerobic or anaerobic
conditions depending on the stabilising compound.

Suitable stabilizing compounds include, for example, hydroquinone, monomethylhydroquinone, anthraquinone,  $\beta$ -nitrostyrene, phenothiazine and 2,6-

anthraquinone, β-nitrostyrene, phenothrazine and 2,0 di-tert-butyl-4-methyl-phenol (BHT).

The esterification reaction may take place in

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the presence of a catalyst. Suitable catalysts include strong acids, for example, sulphur-containing organic acids like alkane sulphonic acids and methane sulphonic acid.

Suitable unsaturated carboxylic acids include, for example, (meth)acrylic acid and derivatives, crotonic acid, (semi-ester of) itaconic acid, maleic acid, citaconic acid, mesaconic acid and fumaric acid.

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Suitable  $\beta$ -hydroxyalkylamides include, for example, N,N'-bis(di- $\beta$ -hydroxyethyl)-1,6-hexanediamide, N-di- $\beta$ -hydroxyethyl acetamide, N,N-bis(di-p-hydroxypropyl)-1,6-hexanediamide, N-di- $\beta$ -hydroxypropyl acetamide, N-di- $\beta$ -hydroxyethyl benzamide and N-di- $\beta$ -hydroxypropyl benzamide. The compound applied in the invention can also be obtained by the reaction between of a  $\beta$ -hydroxyalkyl amide and an unsaturated carboxylic acid chloride, anhydride or ester.

The reaction between the amide and the

unsaturated chloride or anhydride preferably takes

place at temperature between 0°C and 30°C in a solvent

in the presence of a base. Suitable solvents include,

for example, tetrahydroferan, water, dichloromethane or

diethylether. Suitable bases include, for example,

pyridine or triethylamine.

Suitable chlorides, anhydrides or esters include the chlorides, anhydrides and esters of the in the foregoing mentioned carboxylic acid.

The reaction between the amide and the

unsaturated ester, preferably, takes place at
temperatures between 80°C and 140°C in the presence of
a Lewis acid.

Preferably, an excess of the unsaturated ester is applied. The ester functions both as solvent and as reactant.

Suitable Lewis acids are, for example, tetra alkyl titanate and sulphuric acid.

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Another process for the preparation of the compound applied in the invention is the reaction between an oxazoline and an unsaturated carboxylic acid.

Such a reaction can, for example, take place between 50°C and 140°C.

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Suitable oxazolines include, for instance, oxazoline and  $(C_1\text{-}C_{20})$  alkyloxazolines, for instance, ethyl oxazoline and undecyloxazoline.

Suitable unsaturated carboxylic acids include, for example, (meth)acrylic acid and derivatives, crotonic acid, (semi-ester of) itaconic acid, maleic acid, citaconic acid, mesaconic acid and fumaric acid. Preferably, methacrylic acid and acrylic acid are used.

The compound applied in the invention can be cured by means of a free-radical reaction. In these reactions the free radicals can be obtained by radiation initiation.

Radiation-curing preferably takes place by means of, for example, a photochemical process such as, for example, ultraviolet radiation (UV) or a radiation-chemical process such as electron beam (EB).

UV and EB radiation are explained in greater detail by for example Bett et al. in the article entitled "UV and EB curing" (Jocca 1990 (11), pages 446 - 453).

The amount of the compound according to formule (I) can range between 0,01% by weight and 100% by weight in the composition according to the invention.

Generally, the radiation curable composition according to the invention is substantially solvent free.

The composition according to the invention can be used, for example, in coating compositions, inks and adhesives.

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If desired and depending on the application, the compound can be combined with oligomers or polymers which are based, for example, on (meth)acrylate units, maleate units, fumarate units, itaconate units, vinylester units and/or vinylether units.

Due to the relatively high cure speeds the present compounds can also be applied as additives for enhancing the cure speed of a formulation. In general such additives are used in amounts ranging between 0,01% and 25% by weight and preferably in amounts between 0,5% and 10% by weight relatively to the total amount of all ingredients.

After curing the coatings according to the invention have many desired properties such as for example good chemical properties (resistance to solvents, acids, alkalis and moisture), good optical properties and appearance, good mechanical properties (such as hardness, flexibility, adhesion, abrasian resistance, strength and durability), good thermal stability and good weatherability.

The composition comprising the radiation curable binder composition may further comprise pigments, stabilisers and other additives.

The radiation curable formulation generally consists of a prepolymer, a reactive diluent and additives. Two other possible components, depending upon the type of formulation and cure mechanism are pigments and photoinitiator system.

The composition can be applied as a water based coating, as a solvent based coating, as a high solids coating and as a 100% solids coating.

According to a preferred embodiment of the invention the composition is applied as a powder coating.

35 The ester applied in the present invention can also be used as a crosslinker in powder coating compositions if the compound is composed in such a way

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that the softening point (glass transition temperature or melting point) is sufficiently high to be used in this application. Generally, this temperature has to be higher than 40°C.

The most preferred irradiation source is ultraviolet light. Ultraviolet light is preferably high intensity light to provide a dosage to achieve reasonable curing rates. In the event that lower energy light is to be applied, it may then be desired to subject the compositions also to elevated temperatures in order to reduce the time for adequate polymerization to occur.

With respect to UV curing equipment we refer to, for example, pages 161-234 of Chemistry and Technology of UV and EB-formulations, Volume 1, Oldring, 1991.

Suitable lamps employed to provide the desired high intensity and availability of wavelength and spectral distribution include for example that available from Fusion Systems, Corp.

A composition according to the present invention can be applied on substrates such as, for example, plastic, paper, board, leather, glass, wood and metal.

25 This composition is preferably polymerised in the presence of a photoinitiator but it is also possible to polymerise in the absence of a photoinitiator.

Suitable photoinitiators allow for initiation
of the curing process with exposure to light having
wavelengths between about 200 nm and about 600 nm.
Suitable photoinitiators have ketone functionalities
and can be aromatic such as, for example, benzophenone.
Darocur 1173® (Ciba) is a suitable benzyl-ketal-based
photoinitiator, which contains 2-hydroxy-2-methyl-1phenylpropane-1-one as an active component. Irgacure
184® (Ciba) is an aryl ketone containing

hydroxycyclohexyl phenyl ketone as active component, and is a suitable photoinitiator. Irgacure 369® (active component 2-benzyl-2-dimethylaminol-1-(4morpholinophenyl)-butanone-1) is also suitable. Acyl phosphines, such as for example 2,4,6,-trimethylbenzoyl diphenyl phosphone oxide (Lucerine TPO®, BASF) can also be used, as can Quantacure CPTX® (Octel Chemicals), which contains 1-chloro-4-propoxy thioxanthone as active component. Chemical derivatives of these photoinitiators are suitable, as are mixtures of these 10 photoinitiators. A suitable combination of photoinitiators is Irgacure 1800™ (Ciba) consisting of 75% by weight Irgacure 184™ and 25% by weight (bis-(2,6-dimethoxy benzoyl)-2,4,4-trimethylpentyl fosfine oxide). Other suitable photoinitiators can be of the 15 Norrish-II-type, for example, the combinations benzophenone with amine, maleimide with amine, thioxantone with amine and antrachinon with amine.

The invention is explained by reference to the following non-restrictive experiments and examples.

In the following the cure behaviour monitored with "real time infra red spectroscopy". The conversion of the double bonds during the photopolymerisation was monitored by means of infrared (Bruker IFS55).

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#### Experiment I

# Preparation of N-acryloxyethylundecylamide

51.99 g acrylic acid and 0.3 g BHT were heated in a round-bottom flask to 80 °C. Under stirring, 81.3 g molten undecyl oxazoline was slowly added during 1 hour maintaining the reaction temperature at 80 °C. After stirring for another hour at 80 °C the reaction mixture was poured into 200 ml diethyl ether and washed with water, twice with a 10% sodium bicarbonate solution and twice with water. After drying on magnesium sulfate, filtration and evaporation in vacuo of the solvent 100.5 g of N-

acryloxyethylundecylamide was obtained.

#### Example I

#### Curing of a mixture comprising N-

#### 5 acryloxyethylundecylamide

0.99 g of N-acryloxyethylundecylamide according to Experiment I and 0.01 g of Irgacure  $184^{\text{TM}}$  were homogenously mixed at room temperature. This mixture was applied as a 10  $\mu\text{m}$  thick film on a gold coated alumina plate.

Subsequently this plate with the film was irradiated in the infrared machine with a dose of  $500 \, \text{mW/cm}^2$  and the conversion of the double bonds was monitored:

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- maximum rate of polymerization
- 35.5 mol kg<sup>-1</sup>s<sup>-1</sup>

- time for 90% conversion

0.3 sec

#### 20 Comparative Example A

#### Curing of a mixture comprising dodecyl acrylate

0.99 g of dodecyl acrylate and 0.01 g of Irgacure  $184^{\text{TM}}$  were homogeneously mixed at room temperature. This mixture was applied as a  $10\,\mu\text{m}$  thick film on a gold coated alumina plate.

Subsequently the plate with the film was irradiated in the infrared machine with a dose of 500mW/cm² and the conversion of the double bonds was monitored;

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- maximum rate of polymerization
- $1,5 \text{ mol kg}^{-1}\text{s}^{-1}$
- time for 90 % conversion

3.32 sec

Example I and Comparative Example A clearly indicate
that the maximum rate of polymerisation of the
composition according to the invention is higher.

#### Example II

# Curing of a mixture comprising 1% N-acryloxyethylundecylamide and dodecylacrylate

0.01 g of N-acryloxyethylundecylamide according to Experiment I, 0.99 g dodecyl acrylate and 0.01 g of Irgacure 184™ were homogeneously mixed. A  $10\,\mu\mathrm{m}$  thick film was put on a gold coated alumina plate.

Subsequently this plate with the film was irradiated in the infrared machine with a dose of 10 500mW/cm2 and the conversion of the double bonds was monitored:

1,87 mol kg<sup>-1</sup>s<sup>-1</sup> - maximum rate of polymerization 2.59 sec - time for 90 % conversion 15

#### Example III

# Curing of a mixture comprising 2% N-acryloxyethylundecylamide and dodecylacrylate

0.02 g of N-acryloxyethyl-undecylamide 20 according to Experiment I, 0.98 g dodecyl acrylate and 0.01 g of Irgacure 184™ were homogeneously mixed at room temperature. A  $10\,\mu\mathrm{m}$  thick film was put on a gold coated alumina plate.

Subsequently this plate with the film was 25 irradiated in the infrared machine in a infrared machine with a dose of 500mW/cm2 and the conversion of the double bonds was monitored.

- maximum rate of polymerization: 1,96 mol kg<sup>-1</sup>s<sup>-1</sup> 30 2.33 sec - time for 90 % conversion:

### Example IV

# Curing of a mixture comprising 5% N-

acryloxyethylundecylamide and dodecylacrylate 35 0.05 g of N-acryloxyethylundecylamide according to Experiment I, 0.95 g dodecyl acrylate and

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0.01 g of Irgacure  $184^{\text{TM}}$  were mixed. A  $10\,\mu\text{m}$  thick film was put on a gold coated alumina plate.

Subsequently this plate with the film was irradiated in the infrared machine with a dose of 5 500mW/cm² and the conversion of the double bonds was monitored:

- maximum rate of polymerization

2,24 mol kg<sup>-1</sup>s<sup>-1</sup>

- time for 90 % conversion

2.2 sec

#### Example V 10

# Curing of a mixture comprising 10% Nacryloxyethylundecylamide and dodecylacrylate

0.10 g of N-acryloxyethylundecylamide according to Experiment I, 0.90 g dodecyl acrylate and 0.01 g of Irgacure  $184^{\text{TM}}$  were homogeneously mixed at 15 room temperature.

A 10µm thick film was put on a gold coated alumina plate. Subsequently this plate with the film was irradiated in the infrared machine with a dose of 500mW/cm² and the conversion of the double bonds was monitored:

- maximum rate of polymerization 2,66 mol kg<sup>-1</sup>s<sup>-1</sup>

- time for 90% conversion

1.93 sec

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#### Experiment II

#### Preparation of ethylamide ethylacrylate

Experiment I was repeated with the exception that instead of undecyloxazoline 2-ethyl-2-oxazoline was applied.

#### Experiment III

# Preparation of N, N-bis $(\beta$ -hydroxyethyl) acetamide

315 g of diethanolamine were dissolved in 500 g of tetrahydrofuran in a round-bottom flask. Then, 310 35 g of acetic anhydride were slowly added. The temperature was kept below 5°C with the aid of a

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cooling bath. When, after the dropwise addition, exothermic heat was no longer detectable, heating was slowly carried out to 100°C. Tetrahydrofuran and acetic acid were removed under vacuum.

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#### Experiment IV

# Preparation of N, N-bis(β-acryloxyethyl) acetamide

to Experiment III, 300 grams of toluene, 0.05 gram of hydroquinone monomethyl ether and 147 grams of acrylic acid were combined in a round-bottom flask (1 litre). The solution was azeotropically distilled for 9 hours. After cooling to room temperature, the excess acrylic acid was neutralized with a saturated solution of sodium bicarbonate in water and the pH was adjusted to 12. After separation of the water layer and the toluene layer, the water layer was again extracted with toluene. The combined toluene layers were dried by distilling under vacuum.

#### Experiment V

# Preparation of N,N',N,N'-tetrakis( $\beta$ -acryloxyethyl)-1,6-hexanediamide

Experiment IV was repeated with the exception that 320 grams of N,N'-bis(di-β-hydroxyethyl)-1,6-hexanediamide (Primid® XL 552; Rohm & Haas) and 432 grams acid of acrylic acid were mixed in order to obtain N,N',N,N'-tetrakis(β-acryloxyethyl)-1,6-hexanediamide.

#### Example VI

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Curing of a mixture comprising ethylamide ethylacrylate 0.99 g of ethylamide ethylacrylate according to Experiment II and 0.01 g of Irgacure  $184^{\text{TM}}$  were homogenously mixed at room temperature. This mixture was applied as a 10  $\mu\text{m}$  thick film on a gold coated

alumina plate.

Subsequently this plate with the film was irradiated in the infrared machine with a dose of 500mW/cm² and the conversion of the double bonds was monitored:

maximum rate of polymerization

46.6 mol kg<sup>-1</sup>s<sup>-1</sup>

- time for 90% conversion

0.3 sec

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#### Example VII

Curing of a mixture comprising N, N-bis- $(\beta$ acryloxyethyl) acetamide

0.99 g of N,N-bis-( $\beta$ -acryloxyethyl)acetamide according to Experiment IV and 0.01 g of Irgacure 184™ were homogenously mixed at room temperature. This mixture was applied as a 10  $\mu$ m thick film on a gold coated alumina plate.

Subsequently this plate with the film was irradiated in the infrared machine with a dose of 20 500mW/cm² and the conversion of the double bonds was monitored:

- maximum rate of polymerization 46,0 mol kg<sup>-1</sup>s<sup>-1</sup>

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For the calculations of the rates when molecules with functionalities higher than 1 are used, the molecular weight per acrylate unit is defined as the total molecular weight of the molecule divided by the number of acrylate functionalities.

#### Example VIII

# Curing of a mixture comprising N, N', N, N'tetrakis (acryloxyethyl) 1, 6-hexanediamide

0.99 g of the diamide according to Experiment V and 0.01 g of Irgacure  $184^{TM}$  were homogenously mixed at room temperature. This mixture was applied as a 10  $\mu$ m thick film on a gold coated alumina plate.

Subsequently this plate with the film was irradiated with a dose of 500mW/cm² and the conversion of the double in the infrared machine bonds was monitored:

- maximum rate of polymerization 45,5 mol kg<sup>-1</sup>s<sup>-1</sup>

The examples VI-VIII show that the acrylate polymerisation is a fast polymerisation which is less dependent on the functionality.

#### Example IX-X

#### 20 Coating

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The compounds according to the Experiments V and VI were mixed with 1.5% by weight of Darocur $^{\circ}$  1173 (Ciba Geigy), after which a 50  $\mu m$  thick film was deposited on glass.

This film was cured with UV light using a medium pressure mercury lamp. The properties of the cured coatings were determined (see Table I).

The pendulum hardness is determined according to König.

The tensile strength is determined according to DIN535504.

The elongation at break is determined according to DIN53504.

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TABLE 1

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		IX	х
5	Minimum UV dosage necessary for hard coating in mJ/cm <sup>2</sup> (IL 390-A light bug)	600	200
	UV dosage necessary for scourable coating in mJ/cm <sup>2</sup> (IL 390-A light bug)	900	600
10	König surface hardness (sec)	87	119
	Tensile strength (N/mm²)	34 ± 1	31 ± 1
	Elongation at break (%)	4.0 ± 0.3	1.7 ± 0.3

Both coatings were found to have a good resistance to water, N-methylpyrolidone, ammonia, detergents, aqueous citric acid solutions and coffee.

Table I shows that coatings according to the invention have good properties after radiation curing. It is possible to obtain films with good combinations of tensile strength and elongation which will result in tough films.

#### CLAIMS

- 1. A radiation curable composition comprising a mono or multi valent carboxylic ester of a  $\beta$ -hydroxyalkylamide group containing compound, in which the carboxylic ester is derived from an  $\alpha, \beta$ -ethylenically unsaturated carboxylic acid.
  - 2. Composition according to Claim 1, characterized in that the compound is according to formula (I):

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where:

A = hydrogen, or a monovalent or polyvalent organic group which is derived from a saturated or an unsaturated  $(C_1-C_{60})$  alkyl group, or derived from an  $(C_6-C_{10})$  aryl group,

 $Y = hydrogen, a (C_1-C_8)$  alkyl group or

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R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> are, identical or different, hydrogen or a lineair, branched or cyclic (C<sub>1</sub>-C<sub>8</sub>) alkyl

35 chain, R<sup>5</sup>= hydrogen, (C<sub>1</sub>-C<sub>5</sub>)alkyl, -CH<sub>2</sub>OH or CH<sub>2</sub>COOX,

R<sup>6</sup>, R<sup>7</sup> = hydrogen, (C<sub>1</sub>-C<sub>8</sub>)alkyl, (C<sub>6</sub>-C<sub>10</sub>)aryl or COOX

X = hydrogen or (C<sub>1</sub>-C<sub>8</sub>) alkyl and

p = 1 or 2

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- 3. Composition according to Claim 2, characterized in that A is a monovalent organic group derived from a saturated  $(C_1-C_{12})$  alkyl group or A is a polyvalent organic group derived from a saturated  $(C_2-C_{10})$  alkyl group or a  $C_6$ -aryl group.
- 4. Composition according to any one of Claims 2-3, characterized in that Y is hydrogen or methyl,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrogen or methyl,  $R^5$  is hydrogen or (m) ethyl and  $R^6$  and  $R^7$  are hydrogen.
- 10 5. Composition according to any one of Claims 1-4, characterized in that the number average molecular weight of the compound is between 140 and 2500.
  - 6. A radiation curable coating composition comprising a compound as described in any one of claims 1-5.
- 15 7. Coating obtained by radiation curing of a composition according to Claim 6.

AMENDED CLAIMS

[received by the International Bureau on 18 May 1998 (18.05.98); original claims 1-7 replaced by amended claims 1-5 (2 pages)]

A radiation curable coating composition comprising a mono 1. or multi valent carboxylic ester of a  $\beta$ -hydroxyalkylamide group containing compound, in which the carboxylic ester is derived from an  $\alpha, \beta$ -ethylenically unsaturated carboxylic acid, characterized in that the compound is according to formula (I):

$$A \begin{bmatrix} O & Y & R^{1} & R^{3} & O & R^{5} & R^{6} \\ | & | & | & | & | & | & | & | & | \\ - & C & - & N & - & C & - & C & - & C & - & C & = & C \\ & & & | & & | & & | & | & | & | \\ & & & R^{2} & & R^{4} & & & & R^{7} \end{bmatrix}$$

$$P$$

where:

hydrogen, or a monovalent or polyvalent organic A =group which is derived from a saturated or an unsaturated  $(C_1-C_{60})$  alkyl group, or derived from an  $(C_6-C_{10})$  aryl group,

Y = hydrogen, a  $(C_1-C_8)$  alkyl group or

 $\mathbb{R}^1$ ,  $\mathbb{R}^2$ ,  $\mathbb{R}^3$ ,  $\mathbb{R}^4$  are, identical or different, hydrogen or a lineair, branched or cyclic  $(C_1-C_8)$  alkyl chain,  $R^5$ = hydrogen, (C<sub>1</sub>-C<sub>5</sub>) alkyl, -CH<sub>2</sub>OH or CH<sub>2</sub>COOX,  $R^6$ ,  $R^7$  = hydrogen,  $(C_1-C_8)$  alkyl,  $(C_6-C_{10})$  aryl or COOX

# AMENDED SHEET (ARTICLE 19)

 $X = hydrogen or (C_1-C_8)$  alkyl and p = 1 or 2

- 2. Composition according to Claim 1, characterized in that A is a monovalent organic group derived from a saturated  $(C_1-C_{12})$  alkyl group or A is a polyvalent organic group derived from a saturated  $(C_2-C_{10})$  alkyl group or a  $C_6$ -aryl group.
- 3. Composition according to Claims 1-2, characterized in that Y is hydrogen or methyl,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrogen or methyl,  $R^5$  is hydrogen or (m)ethyl and  $R^6$  and  $R^7$  are hydrogen.
- 4. Composition according to any one of Claims 1-3, characterized in that the number average molecular weight of the compound is between 140 and 2500.
- 5. Coating obtained by radiation curing of a composition according to any one of Claims 1-4.

# INTERNATIONAL SEARCH REPORT

Interr 1al Application No PCT/NL 98/00035

A. CLASSIF IPC 6	CO9D4/00 CO8F220/36 CO7C233/0	00	
According to	International Patent Classification(IPC) or to both national classification	on and IPC	
B. FIELDS !	cumentation searched (classification system followed by classification	symbols)	
IPC 6	CO9D CO8F		
	ion searched other than minimum documentation to the extent that suc	h documents are included in the fields sea	rched
Electronic da	ata base consulted during the international search (name of data base	and, where practical, search terms used)	
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT		
Category:	Citation of document, with indication, where appropriate, of the relev	ant passages	Relevant to claim No.
X	EP 0 685 535 A (UCB SA) 6 December see claims 1,2	r 1995	1,6,7
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		/	
X Furt	her documents are listed in the continuation of box C.	X Patent family members are listed	in annex.
"A" docum consu "E" earlier filling "L" docum which citatic "O" docum	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international date ent which may throw doubts on priority claim(s) or is cited to establish the publicationdate of another on or other spacial reason (as specified) enterties the publication of the process	"T" later document published after the inte or priority date and not in conflict with cited to understand the principle or the invention "X" document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an indocument is combined with one or ments, such combination being obvious."	the application but eory underlying the claimed invention t be considered to current is taken alone claimed invention ventive step when the ore other such docu-
*P* docum	means lent published prior to the international filling date but than the priority date claimed	in the art. "&" document member of the same patent	
Date of the	actual completion of the international search	Date of mailing of the international sea	arch report
1	15 April 1998	29/04/1998	<del></del>
Name and	mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  Fax: (+31-70) 340-3016	Authonzed officer  Bettels, B	

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Intern al Application No PCT/NL 98/00035

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Y	EP 0 448 399 A (MINNESOTA MINING & MFG) 25 September 1991 see example 7 see claims 1-4,8,9	1-7
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